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Observation of unique pressure effects in the combination reaction of benzyl radicals in the gas to liquid transition region

Kawon Oum,* Kentaro Sekiguchi, Klaus Luther and Jürgen Troe

Institut für Physikalische Chemie, Universität Göttingen, Tammannstraße 6, D-37077 Göttingen, Germany. E-mail: koum@gwdg.de; Fax: +49 551 393150; Tel: +49 551 3912598

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The combination reaction of two benzyl radicals has been studied in a wide range of pressures (0.01–1000 bar) and temperatures (250–400 K) in various bath gases (Ar, N_2 and CO_2). The measured second-order combination rate constants of benzyl radicals were independent of the pressure and the bath gas below 1 bar, as expected for a limiting "high pressure" rate constant of a termolecular combination process. However, the reaction becomes steadily faster when the pressure in Ar is further raised until it finally starts to decrease when densities corresponding to diffusion controlled kinetics are reached. Such a unique pressure dependence was more strongly accentuated in CO_2 and at lower temperatures. Our results seem to provide first clear indications for a contribution of the radical–solvent interaction in the combination reaction kinetics of such large radicals as benzyl in the gas to liquid transition range.

Introduction

Combination reactions of radicals in the gas phase show a characteristic pressure dependence, also well known for the reverse process, *i.e.* unimolecular dissociation: Linear pressure dependence of the rate constants at "low" pressures is followed by the "fall-off" transition regime leading into the "high" pressure range with a constant, limiting value, k_∞, independent of the density and nature of the bath gas. For large radicals this constant value "k_∞^{ET}" of the so-called energy transfer mechanism is often reached at pressures far below 1 bar. Thus a broad plateau over orders of magnitude in pressure is expected with k equal to k_∞^{ET} until densities are so high that diffusion of the reactants begins to play a role and slow down the reaction rate. The combination reactions of large radicals therefore provide an excellent testing ground for additional bath gas (solvent) effects on the reaction kinetics, beyond that of energy transfer in Markovian binary collisions responsible for the pressure dependence mentioned above. Basic features may be studied under pure gas phase conditions at temperatures far above the critical value and densities reaching far into the range of typical liquids. Suitable choice of bath media/solvents and temperature should allow one to identify additional effects occurring only under typical supercritical conditions or really close to the critical point. As a prototype of such studies, the combination reaction of benzyl radicals ($C_6H_5\dot{C}H_2$) has been chosen:

$$C_6H_5\dot{C}H_2 + C_6H_5\dot{C}H_2 \rightarrow C_{14}H_{14} \qquad k_1 \qquad (1)$$

If there is no significant solvent effect in reaction (1), a transition of the pseudo-second order recombination rate constant k_{rec} (= k_1) from termolecular low-pressure gas-phase behaviour, *via* a broad high-pressure plateau, into the dense fluid diffusion controlled range is expected following eqn. (2):[1,2]

$$k_{rec} \approx \frac{k_{rec}^{g} k_{diff}}{k_{rec}^{g} + k_{diff}} \qquad (2)$$

Here k_{rec}^{g} denotes the recombination rate constant at a given density "in the absence of diffusion control", and k_{diff} is given by the Smoluchowski equation for diffusion-controlled encounters. In liquid solutions, the recombination of benzyl radicals occurs close to the diffusion limit.[3] In the gas phase, Fenter *et al.*[4] and later Boyd *et al.*[5] found that the reaction rates are at the limiting high pressure values in 760 Torr N_2, and almost independent of temperature between 400–450 K[4] and 435–519 K.[5] A mild temperature dependence of the limiting high pressure rate constant, $k_{1,\infty}(T)$, in the range of 700–1500 K, was also observed in a shock wave study.[6]

Reaction (1) was also investigated by Brennecke's group in supercritical CO_2 (70–170 bar) and supercritical ethane (50–120 bar) at two temperatures of 35 and 50 °C.[7] A rapid increase of the recombination rates was clearly observed when the pressure was lowered from an initially higher value towards the critical pressure. The authors interpreted their data only on the basis of diffusion-controlled kinetics by utilizing spin-statistical factors and concluded that there is no indication of an additional increase of the recombination rates due to solvent effects in reaction (1). However, in the present study, we have observed a further increase of the recombination rates in the gas phase at higher pressures of Ar, N_2 and CO_2, when raising the pressure from 1 bar into the critical range or even much higher. In addition a pronounced temperature dependence of such a unique solvent effect in CO_2 was found. In the light of our new results presented here, earlier data from Brennecke and co-workers have to be reinterpreted. Our results strongly suggest that benzyl radical–solvent molecule interactions have a profound influence on kinetics in the gas to liquid transition region.

Experimental

In this study, benzyl radicals were generated from the bimolecular reaction of chlorine atoms with excess amounts of toluene, following the photolysis of molecular chlorine at 308 nm using an excimer laser:

$$Cl_2 + h\nu \ (308 \text{ nm}) \rightarrow 2\,Cl^\bullet \qquad (3)$$

$$Cl^\bullet + C_6H_5CH_3 \rightarrow C_6H_5\dot{C}H_2 + HCl \qquad (4)$$

The temporal behaviour of the benzyl radicals was monitored using the UV absorption technique at 253 nm on time scales of a few milliseconds. A 200 W HgXe lamp was used as a detection light source and the light level was measured by a

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monochromator-photomultiplier arrangement through the high pressure cell (with a spectral band width of *ca.* 2 nm). Premixed gas mixtures of Cl_2, toluene, and the bath gas were compressed in an oil-free diaphragm compressor, and then flowed through the high pressure cell (path length 10 cm and optical diameter 0.9 cm). For experiments below 1 bar, a glass flow cell was used in a separate setup (path length 52 cm and optical diameter 3 cm). Flow rates were controlled by flow meters (Tylan FM361 and FM362) at rates such that reagents and products were removed from the observation volume between laser pulses. Total pressures were measured with high pressure meters (Burster, Model 8201). Two platinum resistance thermometers were directly attached to the front and back side of the cell to measure the temperature. Impurities in the bath gases, especially oxygen, were removed by a series of gas cleaning adsorber (Oxisorb, Messer-Griesheim) and dust filters. All chemicals were purified in a pump–thaw–freezing cycle prior to use. Typical concentration of benzyl radicals was $(1–5)\times10^{13}$ molecule cm^{-3}. Detailed information on our experimental setup can be found elsewhere.[8,9]

Results

We measured second-order combination rate constants (k_1) at various combinations of reaction parameters, such as pressure, temperature, and bath gases. Fig. 1 shows pressure and bath gas dependent rate constants (k_1) at room temperature in a very wide pressure range of 0.01–1000 bar. The observed time dependent UV absorption traces of benzyl radicals at 253 nm were well explained by the second-order kinetic expression of reaction (1) and thus allowed the derivation of k_1. On a longer time scale, the appearance of residual absorptions from products like bibenzyl and benzyl chloride is expected, however their contribution is negligible due to their much smaller absorption coefficients compared to the predominant absorption signal from benzyl radicals. Other side reactions were found to be insignificant.[10]

Rate constants were found to be at the limiting high pressure value of the pure energy transfer (ET) mechanism ($k^{ET}_{1,\infty}$) already at 10 mbar, showing a constant value regardless of the pressure and the nature of the bath gas up to about 1 bar. By averaging the rate constants below 1 bar, a value of

$$k^{ET}_{1,\infty}(T) = (4.1\pm0.3)\times10^{-11}(T/300\ \mathrm{K})^{-0.3}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \qquad (5)$$

was determined. A modest negative temperature dependence of $k^{ET}_{1,\infty}$ was measured in Ar at 5 different temperatures between 275–400 K.[10]

Because of the second order kinetics of reaction (1), the measured reaction rates are sensitive to the absolute initial concentration of benzyl radicals and therefore the value of their absorption coefficients (σ_{benzyl}). Uncertainties in σ_{benzyl} may be one reason for the scatter of $k^{ET}_{1,\infty}$ in previous reports.[4–6] Experimental consistency is thus better checked by comparison of reduced values, $k^{ET}_{1,\infty}/\sigma_{benzyl}$. A value of $\sigma_{benzyl} = 1.3\times10^{-16}$ cm^2 $molecule^{-1}$ was used in this study after wavelength calibration and comparison with a recent gas phase redetermination[11] of $\sigma_{benzyl}(\lambda)$ of the benzyl band with its steep peak near 253 nm, also reported earlier.[12] Possible influences of density- and temperature-dependences of σ_{benzyl} have also to be considered carefully.[10] However, under our experimental conditions, we could not see any unusual behaviour in the UV absorption signals due to spectral shift or unusual changes of the absorption intensities.[10]

Fig. 1 shows steadily increasing rate constants k_1 from 1 bar up to 100 bar in Ar and N_2, followed by decreasing rate constants above 100 bar as the reaction becomes diffusion-controlled. In CO_2, a much larger increase was seen when approaching this pressure regime. In general, the degree of such a unique pressure effect follows a tendency of $CO_2 > Ar \approx N_2 > He$. A salient temperature dependence was observed on this pressure effect, with an enhancement at a lower temperature of 275 K and a correspondingly smaller effect at 350 K, as shown in Fig. 2. Our preliminary data confirm such a unique pressure effect also in CF_3H. A full report on the completed results of this study will follow.[10]

Discussion

It is evident from our current results that there is a solvent-induced pressure and temperature effect in radical combination reaction rates, even in large aromatic radicals like benzyl (see the solid line in Fig. 1, expected when no solvent effect is

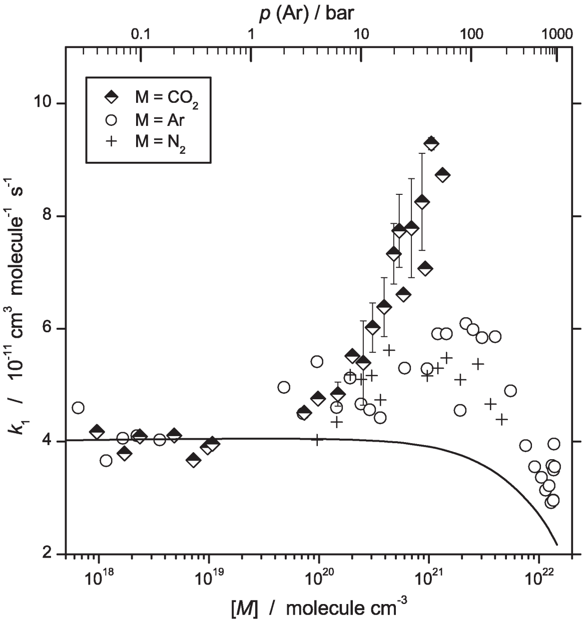

Fig. 1 Density dependent second-order recombination rate constants (k_1) in CO_2, Ar and N_2 at 300 K. The solid line illustrates the expected recombination rates when considering no solvent effects.

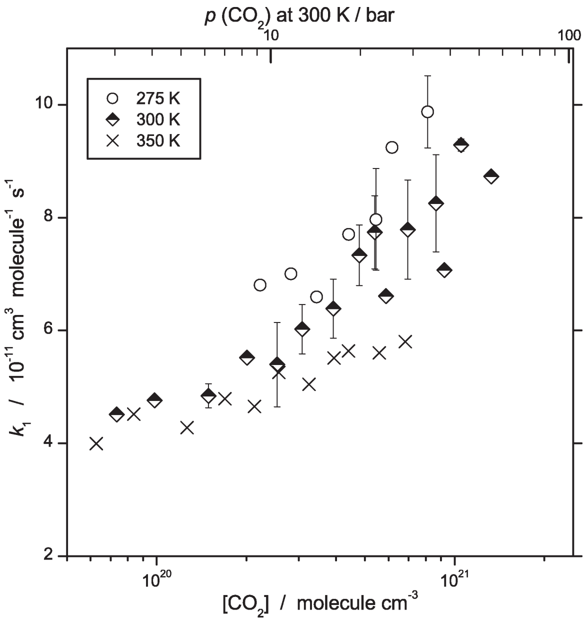

Fig. 2 Density dependent second-order recombination rate constants (k_1) in CO_2 at three different temperatures (275, 300 and 350 K).

considered). It has been believed, especially in the field of supercritical fluids, that radical combination reactions obey diffusion-controlled kinetics without any appreciable solvent effect.[13–16] However, this can not be sufficiently judged without a clear knowledge of the pure gas-phase recombination rate constant "in the absence of diffusion control" ($k_{\rm rec}^{\rm g}$ in eqn. (2)). Experimental data obtained only in the regime of dense fluids do not allow one to tell whether a transition from gas to liquid is smooth or deviates from the expected curve following eqn. (2).

Because rate constants for large radicals such as benzyl are already at the high pressure limit of the energy transfer mechanism below 1 bar, the additional increase of rate constants in the medium density region (before the diffusion-controlled regime) must come from other dynamic features. A most likely candidate, the so-called radical complex mechanism, has been known for a long time and made responsible for unusual gas phase high pressure behaviour in the atom recombination of I_2[17–19] as well as in $O + O_2$,[20] $Cl + O_2$[21] and $F + O_2$.[22] So far it was considered to be relevant only in small molecular systems. Only very recently "turn-ups" from constant values $k_\infty^{\rm ET}$ at increasing high gas densities have been found in combination reactions of slightly larger radicals $ClO + ClO$,[8] $CCl_3 + Br$ and $CCl_3 + CCl_3$.[23] The influence of a radical complex mechanism as well as the possible role of collisional quenching of excited electronic states are discussed in ref. 23. A more detailed analysis of the analogous situation for benzyl as the first case of really large radicals is underway.[10]

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